Tetrahedron 65 (2009) 2599–2604

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Langmuir–Blodgett films of cyclopalladated ferrocenylimine: preparation, characterization, and application in Suzuki coupling reaction

Bing Mu[a,b], Tiesheng Li[a,b,c,*], Chenghuan Li[c], Pingping Liu[a,b], Wei Shang[c], Yangjie Wu[a,b,*]

[a] Department of Chemistry, Key Lab of Chemical Biology and Organic Chemistry of Henan Province, Zhengzhou University, Zhengzhou 450052, PR China
[b] Key Lab of Advanced Nano-information Materials of Zhengzhou, Zhengzhou University, Zhengzhou 450052, PR China
[c] Institute of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, PR China

ARTICLE INFO

Article history:
Received 24 September 2008
Received in revised form 15 December 2008
Accepted 16 December 2008
Available online 3 January 2009

Keywords:
Cyclopalladated ferrocenylimine
Suzuki–Miyaura reaction
Langmuir monolayer
Langmuir–Blodgett (LB) films

ABSTRACT

Langmuir monolayer and Langmuir–Blodgett (LB) films of cyclopalladated ferrocenylimine **1** were prepared and characterized. The surface pressure (π)–area (A) isotherm of complex **1** indicated the formation of highly condensed monolayer on the subphase. Ultraviolet–visible (UV–vis) and Fourier transform infrared (FTIR) spectroscopy showed that complex **1** monolayer was transferred successfully onto solid supports. Atomic force microscopy (AFM) image suggested that LB films transferred on the solid substrate were well-ordered, homogeneous. Cyclic voltammograms of LB films deposited on glassy carbon electrodes showed quasi-reversible oxidation/reduction waves of ferrocene moiety. From the average thickness of monolayer, the hydrocarbon chain could be fairly directed perpendicular to the substrates. Finally, LB films of complex **1** presented a largely improved catalytic efficiency for Suzuki reaction with respect to its cast films and homogeneous reactions under the same conditions. The results might have an implication on the catalytic mechanism of this reaction.

1. Introduction

Palladium-catalyzed cross-coupling reactions such as Heck–Mizoroki arylation, Suzuki–Miyaura reactions, Hartwig–Buchwald amination, and Stille coupling have become an extremely powerful method in organic synthesis for the formation of carbon–carbon or carbon–heteroatom bonds.[1] Among them, the Suzuki–Miyaura cross-coupling reaction has been a common transformation for the formation of carbon–carbon bonds because their products,[2] in particular biaryls, are recurring functional groups in natural products, pharmaceuticals, agrochemicals, ligands for asymmetric synthesis and in new materials, such as liquid crystals.[3] To reach a high degree of efficiency in Suzuki–Miyaura reaction, previous studies mainly focused on the development of new ligands with the steric and electronic properties, notably phosphorus or *N*-heterocycle carbene ligands.[4]

Langmuir–Blodgett (LB) films are built up from a condensed monolayer formed on air–water interfaces by multiple depositions onto solid supports, and the LB method is one of the best ways to prepare thin films with a controlled thickness at a molecular size, well-defined molecular orientation, highly ordered molecular array, known surface coverage, and reproducible interface.[5,6] There are also a variety of experimental techniques that can be employed to characterize, identify, and estimate the nature of the surface species.[7] Therefore, flat surfaces obtained by the LB method offer opportunities to elucidate the molecular structure of the anchored species. Applications of ultrathin films are wide-ranging, and catalysis is in no exception. Until now, there have been few studies of LB films containing amphiphilic organometallic catalysts, which were anchored at the solid surface for catalytic applications. Töllner et al. reported LB films of an amphiphilic rhodium bipyridine complex for the hydrogenation of acetone presented largely improved reaction activity and substrate selectivity with respected to the same complex in solution, demonstrating a major influence of ordered structure on a catalytic reaction.[8] Abatti et al. reported that porphyrin LB films were used in the heterogeneous catalysis of cyclohexene oxidation, furnishing a yield two times higher than that obtained for the homogeneous system, due to a suitable orientation and homogeneous distribution of the catalyst molecules in the LB films.[9] Benítez et al. reported that organized monolayer film of manganese(III) porphyrins prepared by a combination of Langmuir–Blodgett (LB) and self-assembled monolayer techniques showed enhanced activity relative to homogeneous reaction toward the epoxidation of cyclooctene, suggesting immobilization of the catalyst and not only its modified structure, have an important influence on its reaction activity.[10] To the best of our knowledge, no report is found on catalytic applications in coupling reactions using organometallic LB films as catalysts.

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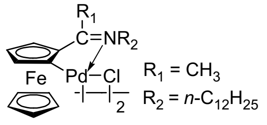
* Corresponding authors. Tel./fax: +86 371 67766667.
E-mail addresses: lts34@zzu.edu.cn (T. Li), wyj@zzu.edu.cn (Y. Wu).

0040-4020/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.tet.2008.12.075

During the past decades we have extensively studied the cyclometalation including cyclopalladation of ferrocenylimine ligands, and cyclopalladated ferrocenylimines obtained have been applied to the coupling reactions.[11] We recently reported the preparation of amphiphilic cyclopalladated ferrocenylimine **1** (Scheme 1) and its catalytic applications in homogeneous Heck and Suzuki cross-coupling reactions at elevated reaction temperature or room temperature.[12,13] One of our interesting attempts was introduction of hydrophobic chains onto cyclopalladated complex to yield amphiphilic catalyst that was expected to form a stable monolayer at the air–water interface. Whether the complex forms LB films successfully is an interesting question. There is no report on LB films prepared from organopalladated catalysts, because they are usually unstable in water. Furthermore, it is interesting to us to study whether LB films of amphiphilic cyclopalladated ferrocenylimine as a catalyst can improve the efficiency of the coupling reactions.



1

Scheme 1. The structure of cyclopalladated ferrocenylimine **1**.

Herein, we first studied the behavior of monolayer of cyclopalladated ferrocenylimine **1** at the air–water interface, and then structurally characterized its LB films on solid substrates by FTIR, UV–vis, and the thickness studies on the molecular orientation, aggregation, and structure at the level of functional groups in LB films. The surface morphology of LB films was directly observed by AFM. Furthermore, the deposition of LB films and the corresponding spin-coated films on ITO substrates allowed a study of their redox behavior by cyclic voltammetry. Finally, the catalytic activity of complex **1** LB films as a catalyst for Suzuki reactions has been examined, and compared to that of the corresponding cast films and homogeneous catalyst under the same conditions.

2. Results and discussion

2.1. π–A Isotherm for cyclopalladated ferrocenylimine 1

Complex **1** having dodecyl chain was spread from a chloroform solution (200 μL, 5×10^{-4} M) on the ultrapure water surface to measure the π–A isotherm at a compression speed of 5 mm/min at 26±1 °C. Figure 1 shows the isotherms prepared by compression after evaporation of solvent for 30 min and stabilization for ca. 1 h in the uncompressed state. The π–A isotherm for complex **1** gave a steep rise in surface pressure and exhibited high collapse pressure 36 mN/m, without phase transition, meaning that highly condensed monolayer was formed. The average surface area occupied per molecule in the monolayer on the water surface of complex **1** was 96 Å^2 by extrapolating the steepest tangent of the isotherm to zero surface pressure.

In order to obtain directly optimum surface pressure for LB films deposition of complex **1** monolayer, the static elasticity of the monolayer film was calculated from π–A isotherm (Fig. 1) by Eq. 1:

$$\mathrm{Es} = -A\frac{d\pi}{dA} \tag{1}$$

The monolayer static elasticity is a measure of the monolayer resistance to a change in area, thus a high static elasticity value is associated with a monolayer that has a strong cohesive structure at the surface and was the most stable, rigid.[14,15] The static elasticity (Es)–surface pressure (π) isotherm of complex **1** monolayer, is shown in Figure 2. The surface pressure obtained at the maximum value of the static elasticity 22 mN/m, was considered as optimum surface pressure of LB films deposition from water surface.

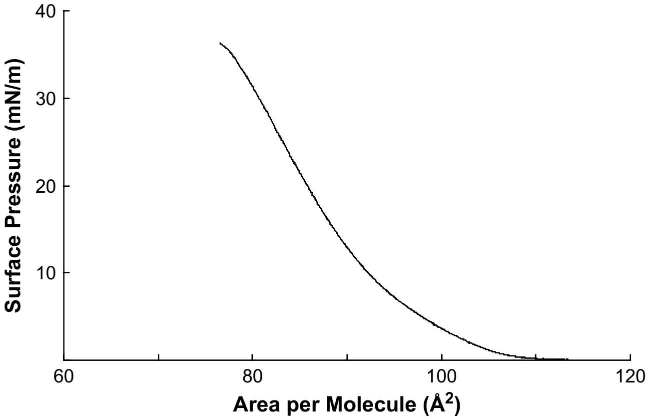


Figure 1. π–A isotherm of complex **1** monolayer at 26±1 °C.

2.2. UV–visible spectroscopy

The UV–vis spectra of complex **1** in CHCl$_3$ solution and in LB films are shown in Figure 3. Usually there are two peaks, ~240 and ~440 nm, in the UV–vis spectra of ferrocene derivatives.[15] A strong, sharp absorption peak was observable with a maximum at ca. 240 nm, which was attributable to the π–π^* electron transition of the ferrocene chromophore of complex **1**. However, the absorption peak in LB films was dramatically shifted to shorter wavelengths compared with that in the solution, suggesting that some interaction among molecules was due to the increase of the π–π^* energy transfer of cyclopentadiene in ferrocene moieties and the close molecular packing such as H-aggregates, viz. the cyclopentadienyl rings of cyclopalladated ferrocenylimine were parallel to each other and tilted in LB films on quartz slides.[16] When the monolayer was transferred onto quartz substrate to form LB films, the shoulder band at ca. 280 nm attributed to the n–π^* electron transition of the ferrocenyl Schiff base chromophore in solution showed a slight red shift, indicating the close packing of the molecules. The linear relationship between the number of layers and the maximal absorbance in the UV–vis spectra indicated that the monolayer was successfully deposited onto solid substrates.

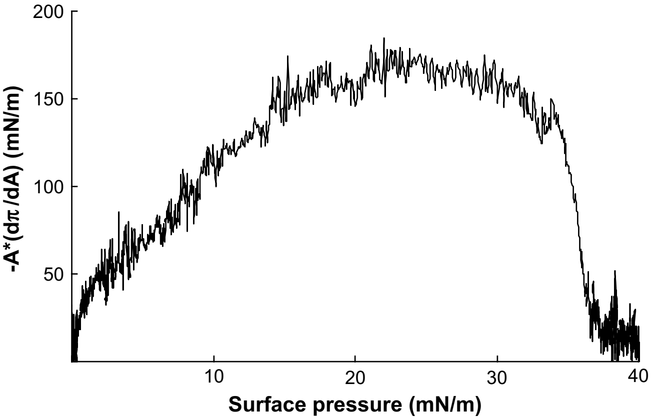


Figure 2. Es–π isotherm of complex **1**.

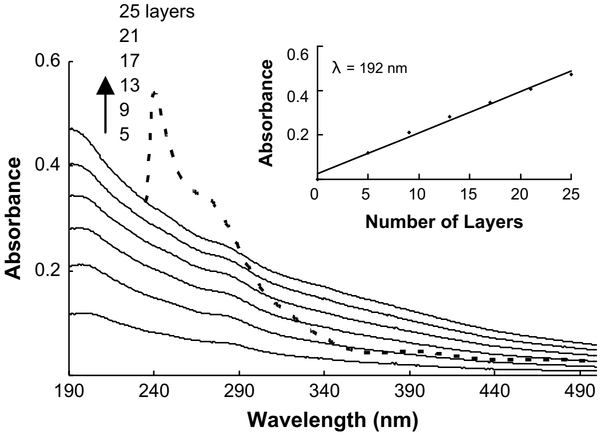


Figure 3. UV–vis absorption spectra of complex **1** in chloroform solution (dotted line) and in LB films with different layers (solid line), and the dependence of UV–vis spectra for LB films on the number of layers deposited.

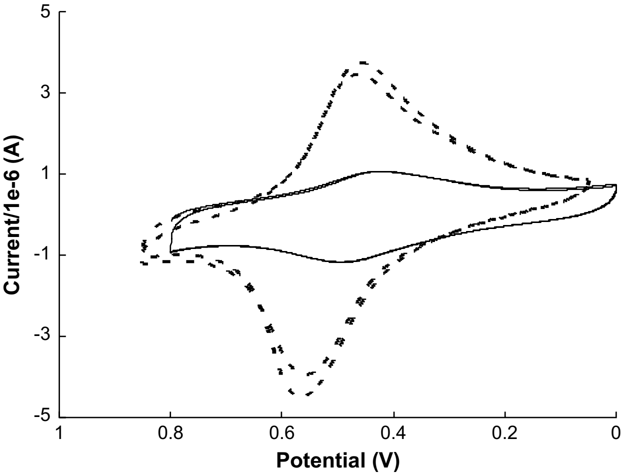


Figure 4. Cyclic voltammograms of complex **1** monolayer LB films (solid line) and cast films (dotted line) deposited on glassy carbon substrates.

2.3. Infrared spectroscopy

IR spectroscopy has proved to be a powerful tool to investigate changes in molecular aggregation, orientation, and structure at the level of functional groups in LB films.[17–19] It is well-known that the wavenumbers of the CH_2 symmetric and antisymmetric modes can be used to monitor the degree of conformational order of the alkyl chain.[20,21] When the hydrocarbon chain is highly ordered (trans-zigzag conformation), the bands due to CH_2 symmetric and antisymmetric modes appear near 2848 and 2918 cm^{-1}, respectively, while, if conformational disorder is induced in the alkyl chain, these bands shift to 2856 and 2927 cm^{-1}, respectively, depending upon the extent of disordering.[22]

In the present case, the vibrational position of the CH_2 antisymmetric and symmetric in 40-layer LB films transferred onto CaF_2 substrate and KBr pellet are similar to each other, and they appeared at ca. 2922 and 2852 cm^{-1}, respectively, suggesting the existence of considerable *gauche* conformations in the hydrocarbon chain. As for cyclopalladated complex **1** in the LB films, only one long hydrocarbon chain resided near the ferrocene moiety so that ample available space could enable it to rotate and tilt, producing some *gauche* conformers in the chain. Therefore, the alkyl chains could not pack densely to each other. The phenomenon is very similar to that Shen et al. previously reported *N*,*N*-dimethylferrocenylmethylhexadecylammonium bromide LB films.[15]

A characteristic C=N stretching band in the region of 1580, 1589 cm^{-1} was observed for the KBr pellet and LB films, respectively, suggesting that the complex maintained its structure in LB films. However, the band shifted to the longer wavenumber in LB films as compared to the KBr pellet. It could be tentatively assumed that dimeric palladacycle underwent dissociation to monomeric form in highly dilute solutions in coordinating solvents already at room temperature.[23,24]

2.4. Electrochemical characteristics

Electrochemical features of complex **1** in LB monolayer film were compared with those in spin-coated films. Figure 4 showed cyclic voltammograms in LB monolayer film and spin-coated films deposited onto glassy carbon electrodes in 0.1 M $KClO_4$ at pH 1.5 at scan rates of 100 $mV\,s^{-1}$. The voltammetric behavior of the LB monolayer film was very similar to that in spin-coated films. All voltammograms showed one quasi-reversible redox process, which was ascribed to the Fc/Fc^+ redox process in thin films. The separation between cathodic and anodic peak potential for the LB monolayer film (ΔE=73 mv) was smaller than that obtained for spin-coated films (ΔE=92 mv), indicating that the rate of electron transfer from the LB films to the electrode and counterion movement in LB monolayer film was fast on the time scale of the experiment.[25–28] This may be correlated with the partial hindrance of the diffusion of the charged species through the spin-coated films due to the formation of aggregates onto glassy carbon electrode, in contrast to the LB monolayer film.[29] Another effect observed was that the half-wave potential E^0 was more cathodic in the monolayer film (E^0=460 mv) than that in spin-coated films (E^0=510 mv), indicating the order arrangement in the LB films facilitated the oxidation of iron(II).

2.5. Atomic force microscopy

AFM can be used to provide topographic images of the LB films, giving a direct view of surface morphology with high spatial resolution, which is often indicative of the film quality.[30] Figure 5 showed AFM image of one-layer LB films of complex **1** transferred

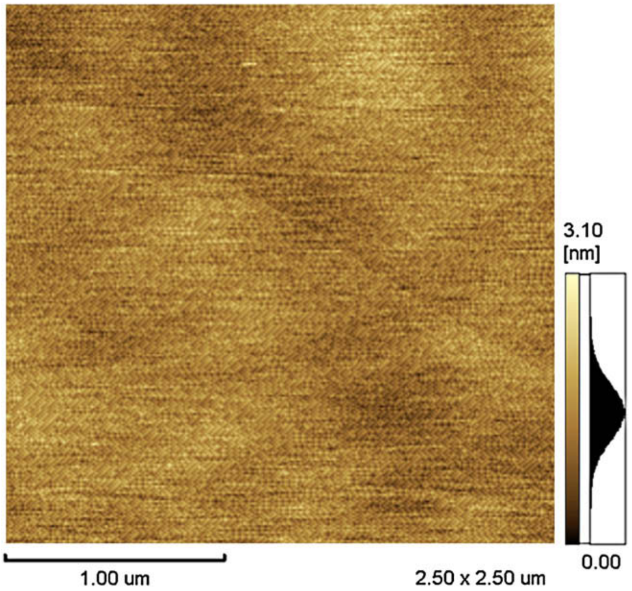


Figure 5. AFM image of one-layer LB films of complex **1** deposited onto freshly cleaved mica at surface pressure of 22 mN/m.

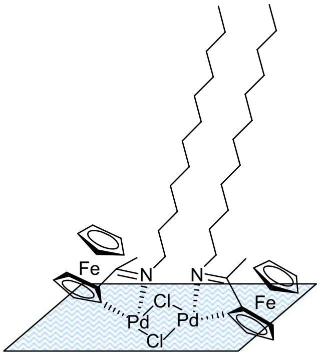


Figure 6. The model of cyclopalladated dimer **1** in LB films.

onto freshly cleaved mica at 22 mN/m surface pressure. The image obtained was smooth and homogeneous, indicating that the well-ordered, uniform monolayer films were fabricated.

2.6. Film thickness

The thickness of the LB films was measured using the Vnkd-8000 optical thickness measurer. The length of the straight dodecyl chain including the C–N and Pd–N bonds is calculated to be 1.9 nm, on the basis of the single crystal data reported by us previously, assuming that the length was the theoretical height of the cyclopalladated complex molecule.[12] Measured average thickness of monolayer in the nine-layer LB films of complex **1** was ca. 2 nm. The result indicated that the alkyl chain was oriented perpendicular to the substrate. Based on the analysis above, we presumed the conformation of cyclopalladated complex **1** in LB films, indicated in Figure 6.

2.7. Suzuki–Miyaura cross-coupling reactions

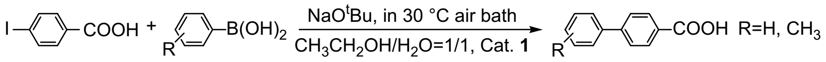
LB films deposited onto solid supports are held together by noncovalent molecule–molecule interactions called the van der Waals forces of attraction. Therefore, in organic solvent or under heating conditions, even with stirring, LB films could be desorbed from substrates, and the ordered structure of LB films was influenced.[8,9] To assess the catalytic properties of LB films of cyclopalladated catalyst in Suzuki coupling reaction, we chose the reaction of 4-iodobenzoic acid with phenylboronic acid as a model reaction in aqueous medium at room temperature.

Initially, we investigated the effect of aqueous solvents, including methanol, ethanol, propanol, isopropanol, butanol, *t*-butanol, pentanol, DMF, DMA, DME, acetonitrile, acetone, dioxane and pure H_2O, and bases (e.g., K_3PO_4, K_2CO_3, Na_2CO_3, $KF\cdot 2H_2O$, KOH, NaO^tBu, KO^tBu) on the reaction of 4-iodobenzoic acid with phenylboronic acid in bulk solution with stirring, at room temperature (0.5 mmol 4-iodobenzoic acid, 0.6 mmol phenylboronic acid and base, with 0.1 mol % **1**, yield determined by HPLC). As a result, NaO^tBu as the base and CH_3CH_2OH/H_2O (1:1) as solvent gave the best result for the reaction.

Under optimal reaction conditions, the LB films of complex **1** transferred onto hydrophilic glass substrates in the reaction 4-iodobenzoic acid with phenylboronic acid exhibited high catalytic activity, yielding 4-biphenylcarboxylic acid as the only observed product [as analyzed by HPLC, yield based on 4-iodobenzoic acid and the product] (Table 1, entries 1–5). With the increase of number of LB films layers, the yields significantly increased, but the turnover numbers changed only slightly. However, Töllner et al. have reported that the catalytic activity of the rhodium complex LB films as catalyst for the hydrogenation of carbon–oxygen double bonds was dependent on the ordered structure and layer orientation, not number of layers.[8] Here, when the upper layer was oriented as head-to-glass, reactions could still carry out, indicating that the alkyl chains of the upper layer did not block the catalytically active centers, and probably their packing was relatively loose to each other in the LB films, in agreement with IR spectroscopy. Moreover, the catalytic films were removed into the same, new reaction after one batch of the reaction, and exhibited very low reaction activity, suggesting desorption of LB films and not truly heterogeneous reaction. LB films of complex **1** showed a significant improvement in catalyst turnovers relative to its cast films and the homogeneous reactions under the same conditions, as shown in Table 1. For the cast films and homogeneous system, only by increasing the loading of catalyst to 1.2×10^{-5} mmol and 8×10^{-6} mmol, respectively, could

Table 1

The cross-coupling reaction of 4-iodobenzoic acid with arylboronic acid catalyzed by catalyst **1** in LB films, cast films, and in solution[a]



Entry	Catalytic systems	Catalyst **1** (10^{-6} mmol)	Yields[b] (%)	TON
1	LB films	2.16 (1 layer)	15	2142
2		4.32 (2 layers)	23	1605
3		6.48 (3 layers)	52	2424
4		8.64 (4 layers)	79	2733
5		10.8 (5 layers)	89 (73)[c]	2478
6	Cast films	8	Trace	—
7		10	19	572
8		12	54	1341
9	Homogeneous	5	Trace	—
10		6	6	314
11		7	13	543
12		8	46	1727
13		9	50	1658
14[d]	LB films	4.32 (2 layers)	37	2569
15[d]	Cast films	6	No reaction	—
16[d]	Homogeneous	4	No reaction	—

[a] Reaction conditions: 4-iodobenzoic acid 0.03 mmol, phenylboronic acid 0.06 mmol, base 0.12 mmol, solvent 3 mL (CH_3CH_2OH/H_2O=1:1), in 30 °C air bath, 48 h without stirring, in weighing bottle (40×25 mm). Cast films, LB films transferred glass slides (25 mm×25 mm×1 mm), homogeneous reaction with blank glass slides.

[b] Yield determined by HPLC, based on 4-iodobenzoic acid and the product in two runs.

[c] Isolated yield (the average value of three times).

[d] 4-Tolyboronic acid.

high turnover number be obtained (Table 1, entries 8 and 12). In addition, the coupling reaction of 4-iodobenzoic acid with 4-tolyboronic acid, catalyzed by two-layer LB films gave the coupling product with 37% yield and 2569 turnover number; however, the coupling reaction catalyzed by cast films or homogeneous catalyst, cannot proceed under the same reaction conditions (Table 1, entries 14–16). The catalytic activity could be highly dependent on the ordered arrangement and homogeneous distribution of the catalyst within LB films. All these results above implied that a quasi-homogeneous mechanism could occur, where firstly Pd^{II} in the LB films was reduced to a Pd^0 species still bound to a substrate surface (possibly by the aqueous alcoholic solvent),[31] then Pd was dissolved as colloids or as complexes that had been leached from LB films, for example, by oxidative addition of a 4-iodobenzoic acid to the substate.[32] Furthermore, synergistic effects may occur as a result of interactions of catalyst molecules in close-packed LB films,[8] which could promote the reduction of Pd^{II} and provide better desorption, leading to faster formation of colloids or complexes in solution. More detailed investigations of the LB films catalytic mechanism are in progress.

3. Experimental section

3.1. Reagents and materials

Solvents were dried and freshly distilled prior to use. The cyclopalladated ferrocenylimine **1** was prepared according to the published procedures.[12] All other chemicals were used as purchased.

3.2. Procedures

Spreading solution was carefully spread onto the ultrapure water surface, and the Langmuir monolayer was compressed after evaporation of solvent for 30 min and stabilization for ca. 1 h in the uncompressed state at a compression speed of 5 mm/min at 26±1 °C. The Y-type LB films were obtained by the vertical lifting method with a transfer ratio close to unity, at a constant surface pressure obtained by the static elasticity (Es)–surface pressure (π) isotherm with a dipping speed of 5 mm/min. LB films were transferred onto CaF_2 substrate (for IR spectroscopy), quartz substrate (for UV–vis spectroscopy and thickness measurements), freshly cleaved mica substrate (for AFM instruments), glassy carbon electrode (for electrochemical study), and glass slide (for catalysis study). The quartz, glass slides on which LB multilayer was deposited were cleaned in boiling concentrated HNO_3, washed with pure water, and then sonicated in ultrapure water for 30 min. Spin-coated films were prepared from chloroform solution of cyclopalladated complex **1** by a spin-coated method with the first step 300 rpm for 6 s and the second step 2000 rpm for 15 s.

3.3. Suzuki reaction

A mixture of 4-iodobenzoic acid 0.25 mmol, arylboronic acid 0.5 mmol, NaO^tBu 1 mmol was transferred to a 25 mL volumetric flask to fix its quantity in aqueous ethanol ($CH_3CH_2OH/H_2O=1:1$). Samples of 3 mL of this mixture were used for 'homogeneous' and 'heterogeneous' runs in weighing bottle (40×25 mm). The heterogeneous reactions contained a glass substrate ($25\times25\times1$ mm^3) with LB films or cast films, while the homogeneous reactions contained a clean glass substrate of the same dimension with a certain amount of **1** (10^{-3} M chloroform solution) added. The reactions were carried out in 30 °C air bath for 48 h without stirring, then the mixture was acidified and the product was extracted by ethyl ether for three times. The combined organic phase was dried with $MgSO_4$, filtrated, and solvent was removed on a rotary evaporator. Crude product was transferred into a 10 mL volumetric flask to fix its quantity in ethyl acetate. The yields were determined by high performance liquid chromatography (HPLC), based on the peak area ratio between 4-iodobenzoic acid and the product. The HPLC conditions were a Kromasil C18 column (150×4.6 mm, 5 μm) with methanol/0.5% acetic acid solution (60:40) as the mobile phase, a flow rate 0.8 mL/min, column temperature 25 °C, UV-detection wavelength 272 nm (phenylboronic acid), 283 nm (4-tolyboronic acid), and the sample size 20 μL. The purified product was identified by ^1H NMR, MS, and melting points with the literature data.

3.3.1. *4-Biphenylcarboxylic acid*

Mp: 223–225 °C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.43–7.45 (m, 1H), 7.49–7.53 (m, 2H), 7.73–7.75 (m, 2H), 7.81 (d, 2H, J=8.3 Hz), 8.03 (d, 2H, J=8.3 Hz), 12.98 (s, 1H). MS: 197.0 $[M-H]^-$.

3.4. Instrumentation

The experiment for monolayer spreading on water was performed on a Langmuir–Blodgett system (KSV-5000-3, KSV Instruments, Helsinki, Finland) equipped with computer controls. Surface pressure was measured with a Pt Wilhelmy plate in air. Distilled and deionized water with resistivity of 18.2 MΩ cm (MILI-Q gradient MILIPORE CO., USA) was used for a subphase. FTIR spectra were recorded on a Bruker VECTOR22 spectrophotometer. UV–vis spectra were recorded with a Lambda 35 UV–vis spectrophotometer (Perkin Elmer Inc. USA). A SPM-9500 J3 (Shimadzu corporation, Japan) was employed for AFM measurements in air at ambient temperature. Electrochemical experiments were carried out with CHI650A electrochemical analyzer. Glassy carbon electrode (ca. 3 mm) with deposited LB films was used as working electrode. The reference electrode was a saturated calomel electrode (SCE), while the counter electrode was a Pt wire. The electrolytic medium was H_2O (Millipore Q-grade, 18.2 MΩ cm) containing 0.1 M $KClO_4$ (pH=1.5). The thickness of the LB films was measured with Vnkd-8000 (Aquila Instrument Ltd. UK). HPLC was conducted on a Waters 600 liquid chromatograph. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. ^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer in DMSO-d_6 with TMS as an internal standard. Spin-coated films were prepared with KW-4A spin coater (Chemat Technology, Inc).

4. Conclusions

The surface behavior of cyclopalladated ferrocenylimine **1** at the air–water interface and transferred onto solid substrates was investigated in detail. The surface pressure (π)–area (A) isotherm indicated highly condensed monolayer was formed. UV–vis spectra suggested the monolayer were transferred successfully onto solid supports, and two dimensional H aggregates were formed. IR spectra indicated that complex **1** maintained its structure in LB films, and hydrocarbon chain attached to palladacycle was packed loosely and, to some extent, was disordered. AFM image showed that LB films transferred on the solid substrate were well-ordered, homogeneous. LB films deposited on glassy carbon electrode showed quasi-reversible oxidation/reduction peaks of ferrocene moiety, and the separation between cathodic and anodic peak potential was small compared with that in spin-coated films. From the average thickness of monolayer, the hydrocarbon chain could stand almost perpendicular to the substrate. Catalytic tests revealed that LB films of complex **1** significantly improved the catalyst turnovers for Suzuki reaction with respect to its cast films and homogeneous reactions under the same conditions. Presently, the preparation of cyclopalladated complexes polymeric LB films and self-assembled monolayer is underway to overcome these weaknesses, such as thermal stabilities or poor resistance to dissolution by organic solvents. Further experiments are needed to gain mechanistic understanding of the reaction and extend them to other coupling reaction.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (No. 20472074), the Innovation Found for Outstanding Scholar of Henan Province (No. 0621001100), the Fund for Outstanding Younger Scholar of Henan Province (074100510015), and the National Natural Science Foundation of Henan Province (0611020100, 2007150042) for their financial support.

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